Dyes and Pigments 146 (2017) 199–202

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

A facile and eco-friendly strategy to prepare synthetic syntans for after-treatment of dyed nylon fabrics

Baofu Guo [a], Dan Li [b], Chao Li [a], Yahong Mao [c], Qingkang Zheng [a, *], Lin Tan [a], Bin Yan [a, *]

[a] *College of Light Industry, Textile and Food Engineering, Sichuan University, Chengdu 610065, China*
[b] *Sichuan Province Fiber Inspection Bureau, Chengdu 610015, China*
[c] *Department of Dyeing and Chemistry, Chengdu Textile College, Chengdu 611731, China*

ARTICLE INFO

Article history:
Received 23 April 2017
Received in revised form
29 June 2017
Accepted 2 July 2017
Available online 3 July 2017

Keywords:
Polyamide
Synthetic syntan
Textile finishing
Acidic dyes
Fastness
Color strength

ABSTRACT

Directly dyed nylon 6, 6 fabrics usually demand recourse to an after-treatment of synthetic tannins (a.k.a. syntans) to improve the fastness of dyeings to water and perspiration. However, the synthesis of commercial syntans requires highly acidic conditions and results in a huge amount of acidic waste effluent after reaction, which has caused severe pollution to the environment. Herein, we report an eco-friendly and feasible strategy to prepare a syntan in one pot in excellent yield *via* the multicomponent reaction of bisphenol S, formaldehyde and sodium phenolsulfonate in aqueous solution using NaOH as catalyst at 100 °C. This strategy can easily obtain a competent syntan bath for after-treatment to the dyed fabrics by dilution and neutralization, while at the same time ensuring much reduced discharge of acidic effluent to the environment after reaction. Compared to current commercial syntans, this new syntan demonstrates a comparable and satisfactory fixing performance on the dyed fabrics in terms of the level of color fastness of the treated fabrics to washing, rubbing, seawater as well as acidic and basic perspiration.

1. Introduction

Polyamide fabrics, such as nylon 6, 6 are usually dyed using acid dyes [1–3]. However, the level of color fastness of these directly dyed samples is often unsatisfactory and insufficient to prevent the dyeings on nylon fabrics from degradation by water and perspiration [3]. Such direct dyeing processes have caused heavy environmental pollution and posed a direct threat to human health [4]. One commonly used strategy to confer the dyed fabrics with adequate fastness to washing is to apply an after-treatment to the dyed fabrics by using the fixing agents, including natural tannins, synthetic tanning agents (i.e., syntans) and syntan/cation systems [5–9]. Among them, the single-stage application of a syntan to the dyed material is the most popular strategy in the textile industries as it does not require any additional fixing treatment and is more convenient to apply compared to natural tannins.

In general, the syntans are synthesized *via* phenol-aldehyde condensation under a strong acidic condition [7,10–12]. To create a highly acidic environment for this reaction, the industries not only use concentrated H_2SO_4 as the catalyst but also select acid anhydrides as the solvent. Obviously, this synthesis protocol suffers certain drawbacks such as prolonged reaction time, high reaction temperature (130–150 °C), use of highly acidic catalysts, burdened reclamation task of anhydride solvents after reaction and generation of a huge volume of acidic waste effluent. Therefore, it is of great importance to introduce an eco-friendly and feasible procedure for the production of the syntans, which could satisfy the following requirements: (1) it adopts green and non-toxic solvents as the reaction medium; (2) its reaction is qualified with moderate temperature, cheap catalyst with high catalytic activity and short reaction time accompanied with excellent yield; (3) only simple or no purification is required for the final product.

Herein, we report an eco-friendly and feasible strategy for the preparation of syntans in excellent yield *via* the multicomponent reaction of bisphenol S, formaldehyde and sodium phenolsulfonate in aqueous solution using NaOH as catalyst at 100 °C. In contrast to the previous strategy, this method is based on a one-pot reaction with the help of activation of a phenol species in a slightly basic aqueous solution and hence it will not cause severe corrosion to the synthesis vessels and is able to scale up easily without further modifications to the existing synthesis facilities. Moreover, the method totally avoids the purification process after reaction and by simply diluting and neutralizing its resulting aqueous solution with

---

* Corresponding authors.

http://dx.doi.org/10.1016/j.dyepig.2017.07.004
0143-7208/

water, it can produce a competent syntan bath directly for after-treatment to the dyed fabrics. Using a commercial syntan as a reference, the new syntan approach demonstrates a comparable fixing performance on the dyed fabrics in terms of the level of color fastness of the treated fabrics to washing, rubbing and seawater as well as acidic and basic perspiration.

2. Experimental

2.1. Materials

Bisphenol S, and sodium phenolsulfonate were purchased from Wu Han Technological Company. Formaldehyde, sodium hydroxide and concentrated sulfuric acid were supplied by Chengdu Clone Chemical Reagent Company. All the chemicals were used as received without further purification.

2.2. Synthesis of Syntan A under alkaline condition

The Syntan A was synthesized *via* a condensation reaction by using bisphenol S, formaldehyde and sodium phenolsulfonate under alkaline condition. One typical example was shown as follows: a mixture of bisphenol S (24.00 g, 95.9 mmol), sodium phenolsulfonate (13.20 g, 67.3 mmol), sodium hydroxide (1.00 g, 25 mmol), and distilled water (50 mL) were placed in a 100 mL three-necked bottom-round flask. The whole system was purged with N_2 for 30 min and then slowly heated up to 100 °C 6 mL of 37 wt % formaldehyde was added dropwise into the system under continuously stirring. After refluxing at this temperature for 2 h, the resultant mixture was cooled to room temperature, which was treated to obtain a syntan bath with the desired pH and concentration and used for direct after-treatment of dyed nylon fabrics. For characterizations, the resulting reaction solution was diluted with water and washed with ethyl ether several times to remove unreacted monomers. The separated aqueous phase was lyophilized to afford the colorless product of Syntan A (41.50 g, 90.50%). FT-IR (neat, cm^{-1}): 3482, 1272 (Ar-OH), 1469 and 691 ($-CH_2-$), 1272, 1118 and 548 (−SO2−) and 902 and 822 (Ar), ^1H NMR (400 MHz, D_2O), δ (ppm): 8.22 (s, $SO_2C_6H_2CH_2C_6\mathbf{H_2}SO_3Na$), 7.95–7.81 (b, $HOH_2C_6\mathbf{H_2}SO_2C_6H_2$), 7.82–7.65 (b, $SO_2C_6\mathbf{H_2}CH_2C_6H_2SO_3Na$), 7.47(b, $HO\mathbf{H_2}C_6H_2SO_2C_6H_2$), 4.67 (s, $SO_2C_6HC\mathbf{H_2}C_6H_2SO_3Na$). UV/Vis (PBS): $\lambda_{max\ (Abs)}$ [nm] (ε [$M^{-1}cm^{-1}$]) = 264 (9700).

2.3. Characterization methods

Fourier transform infrared spectroscopy (FTIR). Infrared spectra of Syntan A samples were recorded in transmission mode on a FTIR - 920 type Fourier infrared spectrometer (London, UK) and reported in terms of frequency of absorption (cm^{-1}). All spectra were collected as a sum of 128 scans in a spectral range from 500 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

Nuclear magnetic resonance (NMR). ^1H NMR spectra were recorded on a Bruker-TM 400 MHz instrument. D_2O was used as solvent to dissolve Syntan A.

High resolution mass spectrometry (HRMS). HRMS analyses were recorded on a BIOTOF IIIQ mass spectrometer. Before MS measurement, the Syntan A sample (50 mg) was dried in a large watch glass at 50 °C for 10 h. MS spectra were then recorded with *m*/*z* scan range from 200 to 800. According to plasma peaks such as [m + 1], [m+ 23] and [m + 39], the molecular weight distribution of Syntan A was calculated based on the reported procedure [13].

2.4. Dyeing

Nylon 6, 6 fabrics were dyed according to a published procedure [14] as shown in Fig. 1a.

2.5. Syntan treatment

The dyed fabric samples were after-treated with the commercial syntan or syntan A in sealed stainless steel dye pots, housed in a Color I5D matching instrument (Ellie color company, USA) using a liquor ratio of 15:1. The details about the whole procedure are shown in Fig. 1b. At the end of treatment, the treated samples were rinsed thoroughly with tap water and allowed to air dry.

2.6. Color fastness testing

The color fastness to washing, rubbing and sea water as well as acidic and basic perspiration were measured according to the standard methods ISO 105-C10:2006, ISO 105-X12:2001, acidic and basic-TS EN ISO 105 E04 and EN ISO 105 E02, respectively.

3. Results and discussion

3.1. Synthesis and characterization of Syntan A

The synthesis route of Syntan A is schematically illustrated in Fig. 2a. It includes three sequential steps of (i) ionizing bisphenol S to make the aromatic groups more nucleophilic, (ii) nucleophilic addition between formaldehyde and anionic biphenol S and (iii) condensation reaction. Compared to the existing procedure for the syntan synthesis under highly acidic conditions, our synthesis route is greener, eco-friendlier and more benign as it not only can directly produce the qualified syntan solution for after-treatment by simply dilution and pH adjustment but also does not generate any strongly corrosive acidic effluent after reaction. Its successful synthesis was confirmed by FTIR and HRMS measurements. As shown in Fig. 2b, the characteristic peaks at 1469 cm^{-1} and 691 cm^{-1} for the $-CH_2$ groups and at 902 cm^{-1} and 822 cm^{-1} for the multi-substituted aromatic rings can be clearly identified, indicating that the condensation reactions between formaldehyde and bisphenol S have occurred. Moreover, the typical peaks ascribing to the $-SO_2-$ groups, found at 1272 cm^{-1}, 1118 cm^{-1} and 548 cm^{-1}, also verified successful incorporation of bisphenol S into the chemical structure of Syntan A. In addition, condensation reactions proceeded completely as no peaks at 1740–1690 cm^{-1} ascribing to formaldehyde were detected, confirming that the Syntan A was prepared in excellent yield. From MS spectra of Syntan A in Fig. 2C, we can conclude that the resulting products were mainly a mixture of linear oligomers with the chemical structure as shown in Fig. 2a, whose polymerization degree was quite low and only varied between 1 and 3. We attributed this result to the reaction conditions we selected. At the reaction condition (i.e., 100 °C for 2 h), the condensation reactions happened in a linear way that prevent formation of a crosslinked network. The finding is consistent with a

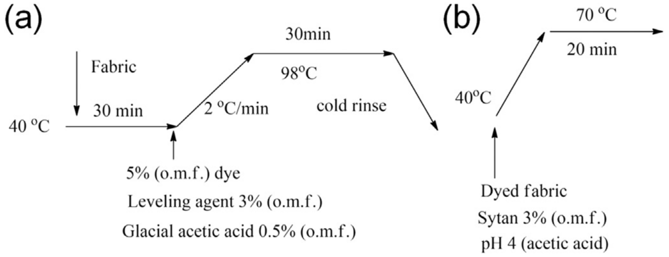

Fig. 1. (a) Dyeing profile for nylon fabrics; (b) After-treatment profile for dyed nylon fabrics.